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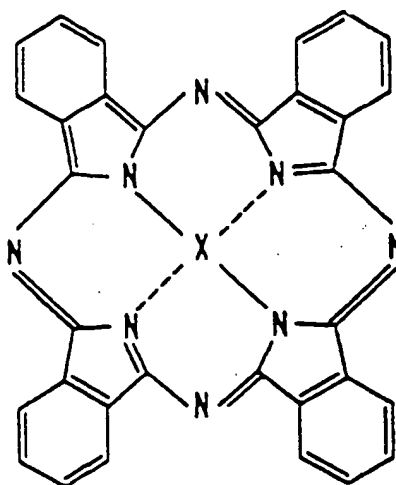
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(54) Method of making an organic thin film transistor and article made by the method

(57) Thin film transistors in which the active layer is an ordered film of a phthalocyanine coordination compound with a field-effect mobility greater than  $10^{-3} \text{ cm}^2/\text{Vs}$  and a conductivity in the range of about  $10^{-9} \text{ S/cm}$  to about  $10^{-7} \text{ S/cm}$  at  $20^\circ\text{C}$  are disclosed. Examples of suitable phthalocyanines include copper phthalocyanine,zinc phthalocyanine, hydrogen phthalocyanine, and tin phthalocyanine. Thin film devices made of these materials have an on/off ratio of at least about  $10^4$ . It is advantageous if the device is fabricated using a process in which the substrate is heated to a temperature in the range of about  $30^\circ\text{C}$  to about  $200^\circ\text{C}$  when the film is formed thereon.

FIG. 1



## Description

## Field of the Invention

5 This invention relates to thin film transistors (TFTs) that contain an active layer of organic material, and to methods for making such transistors.

## Background of the Invention

10 Organic semiconductor materials are currently being investigated for use as the active layer in a variety of devices including light-emitting diodes, nonlinear optical devices, and TFTs such as metal-insulator-semiconductor field effect transistors (MIS-FETs). Organic semiconductor materials offer processing advantages such as compatibility with flexible plastic substrates and ease of application by spin-coating and their use in processes for device fabrication is therefore attractive. However, in order for these materials to be useful for use in TFT devices, the resulting devices  
 15 must have an on/off ratio (of the source/drain current) suited for the particular application. Although devices with on/off ratios as low as 100 are suited for some application, typically TFT devices must have an on/off ratio of at least about  $10^3$ . The properties of the organic semiconductor materials that govern the on/off ratio are carrier mobility and conductivity. Organic semiconductor materials typically have a carrier mobility in excess of about  $10^{-8}$  cm<sup>2</sup>/Vs but less than 1 cm<sup>2</sup>/Vs. Consequently, based upon the relationship between carrier mobility, material conductivity, and device on/  
 20 off ratio, the requisite conductivity of the organic semiconductor material is defined by the carrier mobility of the material and the desired on/off ratio.

A class of doped amorphous organic semiconductors is described in Brown, A.R., et al., "A universal relation between conductivity and field-effect mobility in doped amorphous organic semiconductors," Synthetic Materials, Vol. 68, pp. 65-70 (1994). Brown et al. report a linear relationship between the conductivity and the field effect mobility of  
 25 such material, i.e., as the conductivity increases so does the field-effect mobility. Although Brown et al. report materials with a very high mobility, this high mobility was achieved at the expense of conductivity. Brown et al. conclude that high on/off ratios and high mobilities are not to be expected in devices constructed from amorphous organic semiconductors. Accordingly, if satisfactory devices are to be made from these materials, the field effect mobility and the conductivity of these materials must be within a range that provides a device with an on/off ratio of at least  $10^5$ .

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## SUMMARY OF THE INVENTION

The present invention is directed to a semiconductor TFT device in which the active layer is an organic semiconductor material with a field effect mobility greater than  $10^{-3}$  cm<sup>2</sup>/V-s and a conductivity in the range of about  $10^{-9}$  S/cm  
 35 to about  $10^{-7}$  S/cm. These organic semiconductor materials are coordination compounds of phthalocyanine (referred to herein with the abbreviation Pc) with copper, zinc, tin, or hydrogen. These coordination compounds form ordered films, and exhibit higher field effect mobility at lower conductivities than amorphous, doped phthalocyanine. The present invention is also directed to a process for making these devices.

In one embodiment of the present invention, the device is a MIS-FET type TFT with an active layer of the organic  
 40 semiconductor. Such devices typically have three spaced-apart contacts (e.g. conductive metals such as gold), at least two of which are in physical contact with the semiconductor layer. The third contact is adapted to control the current through the semiconductor layer between the first and second contacts.

The TFT device of the present invention is formed on a conventional substrate material such as glass, silicon or plastic. A layer of dielectric material is formed over the substrate. One of the contacts is physically connected to the  
 45 substrate and the layer of dielectric material is interposed between the other two contacts and the substrate.

In the process of the present invention, the layer of phthalocyanine coordination compound is formed on a heated substrate. The temperature of the substrate is in the range of about 30°C to about 200°C. It is advantageous if the temperature of the substrate is about 125°C to about 175°C.

## 50 BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of the structure of the phthalocyanine coordination compounds of the present invention wherein the ion in the phthalocyanine is indicated generally by the letter X.

FIG. 2 is a cut away side view of a TFT device of the present invention.

55 FIG. 3 illustrates the relationship between the field effect mobility of a Cu-Pc film and the temperature of the substrate on which the film is formed.

## DETAILED DESCRIPTION

The present invention is directed to a TFT device in which the active layer is a phthalocyanine coordination compound and a process for making the device. The device of the present invention has an on/off ratio greater than  $10^4$  at  $20^\circ\text{C}$ . In order to obtain devices with the desired on/off ratio, it is advantageous if the phthalocyanine has a field effect mobility greater than  $10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$  and a conductivity in the range of about  $10^{-9} \text{ S/cm}$  to about  $10^{-7} \text{ S/cm}$ . FIG. 1 is an illustration of a phthalocyanine coordination compound. The coordinate ion is indicated generally by the letter X. It is advantageous if the coordinate ion is either copper, zinc, tin, or hydrogen.

FIG. 2 illustrates a MIS-FET type device according to the invention. The transistor 20 is a substrate 11 over which a layer of dielectric material 13 and a metal contact 15 are formed. Two additional metal contacts, 17 and 19, are formed over the dielectric layer 13. A layer of the phthalocyanine coordination compound 21 is formed over and between the contacts 17 and 19.

The substrate of the above-described device is made of conventional materials such as silicon, glass, or plastic. The contacts are made of a conventional material for this purpose such as gold. The dielectric material is a conventional material such as silicon dioxide, silicon nitride ( $\text{Si}_3\text{N}_4$ ), or aluminum oxide ( $\text{Al}_2\text{O}_3$ ). The contacts and the dielectric layer are formed on the substrate using well known, conventional techniques which are not discussed in detail herein.

By way of example, MIS-FET type TFTs are formed with a  $12 \mu\text{m}$  channel length and a  $250 \mu\text{m}$  gate length on an n-doped silicon substrate. A  $3000 \text{ \AA}$  thick layer of silicon dioxide is formed over the substrate. The silicon dioxide layer functions as a gate dielectric material and has a capacitance of about  $10 \text{ nF/cm}^2$ . Two separate gold contacts are formed over the gate dielectric layer. A film of a phthalocyanine coordination compound is formed over the gate dielectric layer and the contacts formed thereon. The phthalocyanine film is formed on a heated substrate. The temperature of the substrate is in the range of about  $30^\circ$  to about  $200^\circ\text{C}$ . It is advantageous if the substrate temperature is about  $125^\circ\text{C}$  to about  $175^\circ\text{C}$ .

The phthalocyanine film is formed on the substrate using conventional techniques such as vacuum deposition. It is advantageous if the thickness of the phthalocyanine film is about  $500 \text{ \AA}$  to about  $600 \text{ \AA}$ . TFTs so formed have an on/off ratio greater than  $10^4$  at  $20^\circ\text{C}$ .

## Example

Phthalocyanine coordination compounds with platinum (Pt), copper (Cu), zinc (Zn), nickel (Ni), iron (Fe), tin (Sn), and hydrogen ( $\text{H}_2$ ) were obtained from a commercial supplier. For convenience, the phthalocyanine coordination compound is referred to generally as X-Pc, where X is a generic designation for the coordination ion (e.g., Pt, Fe,  $\text{H}_2$ , etc.) These materials were then purified by sublimation at a pressure of less than about  $8 \times 10^{-4}$  Torr and a temperature of about  $380^\circ\text{C}$ . This sublimation procedure was performed three times total.

Devices were formed using the above identified phthalocyanine coordination compounds as the active layer. A layer of phthalocyanine coordination compound 21 was formed on a substrate to form the device 20 depicted in FIG. 2 and described generally above. In the context of this example, the term substrate is used to refer to the structure of a silicon substrate 11 on which is formed a layer of gate dielectric 13 with two contacts 17 and 19 formed thereon. A third contact 15 is formed directly on the silicon substrate.

The temperature of the substrate was controlled during the deposition of each film thereon to determine the effect of substrate temperature on the mobility and conductivity of the phthalocyanine layer. Individual films of each of the above-identified phthalocyanines coordination compounds were formed on substrates heated to temperatures of  $30^\circ\text{C}$ ,  $125^\circ\text{C}$ , and  $200^\circ\text{C}$ . Each film was formed using vacuum deposition in an evaporation chamber at a pressure of  $2 \times 10^{-6}$  torr. About  $50 \text{ mg}$  of the phthalocyanine was placed in a tungsten boat. The boat was placed in a conventional evaporator system. The substrate was also placed in the evaporator on a copper block. A temperature controller was used to control the temperature of the copper block which, in turn, was used to control the temperature of the substrate. The boat was heated to a temperature of about  $380^\circ\text{C}$  and the phthalocyanine film was formed at a rate of about  $4 \text{ \AA}$  to about  $5 \text{ \AA}$  per second.

The field-effect mobility and the conductivity of the various films prepared as described above is enumerated in Table I below. The effect of the substrate temperature during film formation on the field-effect mobility and conductivity of the films is also reported in Table I.

TABLE I

Material	Property	Substrate Temperature		
		$30^\circ\text{C}$	$125^\circ\text{C}$	$200^\circ\text{C}$
	Mobility ( $\text{cm}^2/\text{Vs}$ )	$6.0 \times 10^{-4}$	$2 \times 10^{-2}$	$6.7 \times 10^{-3}$

TABLE I (continued)

Material	Property	Substrate Temperatur		
		30°C	125°C	200°C
Cu-Pc	Conductivity (S/cm)	$1.8 \times 10^{-9}$	$4 \times 10^{-9}$	$3.1 \times 10^{-9}$
	on/off ratio	$3.7 \times 10^4$	$4 \times 10^5$	$1.7 \times 10^5$
Zn-Pc	mobility (cm <sup>2</sup> /Vs)	$2.3 \times 10^{-4}$	$2.4 \times 10^{-3}$	$2.8 \times 10^{-3}$
	conductivity (S/cm)	$1.4 \times 10^{-6}$	$1.1 \times 10^{-8}$	$1 \times 10^{-7}$
	on/off ratio	12	$2.2 \times 10^4$	$2 \times 10^3$
H <sub>2</sub> -Pc	mobility (cm <sup>2</sup> /Vs)	$1.3 \times 10^{-3}$	$2.6 \times 10^{-3}$	$5.6 \times 10^{-7}$
	conductivity (S/cm)	$6.4 \times 10^{-7}$	$2.2 \times 10^{-9}$	$2.1 \times 10^{-9}$
	on/off ratio	160	$8.1 \times 10^4$	26
Sn-Pc	mobility (cm <sup>2</sup> /Vs)	$7.3 \times 10^{-5}$	$3.4 \times 10^{-3}$	not measurable
	conductivity (S/cm)	$1.9 \times 10^{-7}$	$2.4 \times 10^{-8}$	$4.8 \times 10^{-8}$
	on/off ratio	36	$1.6 \times 10^4$	not measurable
Fe-Pc	mobility (cm <sup>2</sup> /Vs)	$3.6 \times 10^{-5}$	$6.9 \times 10^{-4}$	$1.1 \times 10^{-5}$
	conductivity (S/cm)	$5.1 \times 10^{-9}$	$6.8 \times 10^{-7}$	$1 \times 10^{-7}$
	on/off ratio	570	110	100
Pt-Pc	mobility (cm <sup>2</sup> /Vs)	$1.5 \times 10^{-4}$	$1.5 \times 10^{-4}$	$9 \times 10^{-5}$
	conductivity (S/cm)	$2.2 \times 10^{-7}$	$2.7 \times 10^{-7}$	$4.7 \times 10^{-9}$
	on/off ratio	120	80	$2.6 \times 10^3$
Ni-Pc	mobility (cm <sup>2</sup> /Vs)	$7 \times 10^{-6}$	$3 \times 10^{-5}$	$5.4 \times 10^{-5}$
	conductivity (S/cm)	$3.9 \times 10^{-9}$	$6.2 \times 10^{-8}$	$6.4 \times 10^{-9}$
	on/off ratio	120	110	110

The field-effect mobility reported in Table I was calculated using the following equation:

$$I_{DS} = (WC_i/2L)\mu(V_G - V_O)^2$$

where W is the channel width (250  $\mu$ m), L is the channel length (12  $\mu$ m) and  $C_i$  is the capacitance per unit area of the gate dielectric (10 nF/cm<sup>2</sup>). To calculate the field effect mobility,  $\mu$ , using the above-identified equation, the threshold voltage ( $V_O$ ) of the device is determined from the relationship between the square root of the drain-source current ( $I_{DS}$ ) at the saturated region and the gate voltage of the device ( $V_G$ ) by extrapolating from the measured values back to  $I_{DS}=0$ . The  $I_{DS}$  at the saturated region is determined by observing the relationship between the drain-source voltage ( $V_{DS}$ ) and the drain-source current at a given  $V_G$ .  $I_{DS}$  at the saturated region is where  $I_{DS}$  no longer increases with increasing drain-source voltage.  $I_{DS}$  at the saturated region varies with  $V_G$ . This method for determining  $V_O$  is conventional and well known to one skilled in the art.

The field effect mobilities reported in Table I are average values. Devices were formed using two substrates for every material and every temperature reported in Table I. For example, devices with a Cu-Pc film were formed on six substrates total, two at each of the reported temperatures. At least twenty devices were formed on each substrate.

The on/off ratio is the ratio of the drain current ( $I_{D1}$ ) flowing in saturation when  $V_G$  is equal to or greater than the drain voltage ( $V_D$ ) to the  $I_{D2}$  flowing when  $V_G$  is zero. For example, if  $I_{DS}$  is  $8 \times 10^{-5}$  A when  $V_D$  and  $V_G$  are both -100 V and  $I_{DS}$  is  $1 \times 10^{-11}$  A when  $V_G = 0$  and  $V_D = -100$  V, then the on/off ratio of the device is  $8 \times 10^6$ .

Although the inventor does not wish to be held to a particular theory, it is believed that the performance of the device is linked to the morphology of the phthalocyanine films. X-ray diffraction analysis of the films enumerated in Table I shows an increase in order in most of the films (i.e. the films became less amorphous) with an increase in the temperature of the substrate on which the films were formed. The order of the films was determined from the x-ray diffraction trace that results from the (200) lattice planes. A trace with a single peak was indicative of a highly ordered film. The intensity of this peak was observed to increase with an increase in the temperature of the substrate on which the film was formed.

Consequently, it appears that the order of the film is related to the field effect mobility of the material. As observed by the data in Table I, the field effect mobility of most films increased as the temperature of the substrate was increased.

from 30° to 125°C. As noted above, the order of the film also increased with increasing substrate temperature during film formation. However, Table I also shows a decrease in field effect mobility as the substrate temperature during deposition was increased from 125° to 200°C. This effect may be explained by the fact that film discontinuities increase at higher temperatures and these discontinuities have a negative effect on field effect mobility.

The relationship between the temperature of the substrate during film formation and the field effect mobility of a Cu-Pc film is illustrated in FIG. 3. FIG. 3 demonstrates that the field effect mobility of the Cu-Pc film increases dramatically as the temperature of the substrate increases from about 30°C to about 140°C. At substrate temperatures above 140°C, the trend reverses and the field effect mobility decreases with increasing temperature.

## Claims

1. A thin film transistor comprising:
  - a substrate with a layer of a phthalocyanine coordination compound formed thereon and contacts for applying current through the layer of the phthalocyanine coordination compound wherein the phthalocyanine coordination compound has a field-effect mobility greater than  $10^{-3}$  cm<sup>2</sup>/Vs and a conductivity in the range of about  $10^{-9}$  S/cm to about  $10^{-7}$  S/cm at 20°C and wherein the thin film transistor has an on/off ratio of the source drain current that is at least  $10^4$ .
2. The thin film transistor of claim 1 wherein the phthalocyanine coordination compound has a coordinate selected from the group consisting of copper, zinc, hydrogen, and tin.
3. The thin film transistor of claim 2 wherein the layer of phthalocyanine coordination compound has a thickness of about 500 Å to about 600 Å.
4. The thin film transistor of claim 3 wherein the layer of phthalocyanine coordination compound is an ordered layer.
5. The thin film transistor of claim 4 wherein the thin film transistor is a MIS-FET.
6. A process for fabricating a device comprising:
  - forming a layer of an ordered phthalocyanine coordination compound on a substrate heated to a temperature in the range of about 30°C to about 200°C and forming contacts on the substrate for applying current through the layer of ordered phthalocyanine coordination compound.
7. The process of claim 6 wherein the ordered phthalocyanine coordination compound is selected from the group consisting of copper phthalocyanine, zinc phthalocyanine, hydrogen phthalocyanine, and tin phthalocyanine.
8. The process of claim 7 wherein the temperature is about 125°C to about 175°C.
9. The process of claim 8 wherein the device is a thin film transistor.
10. The process of claim 9 wherein the device is a MIS-FET.

FIG. 1

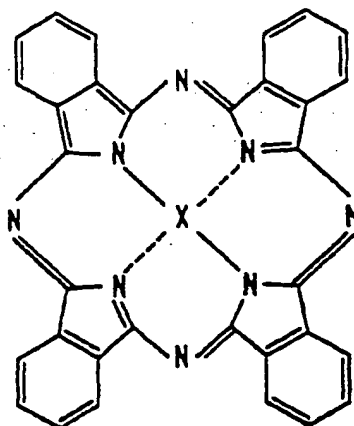


FIG. 2

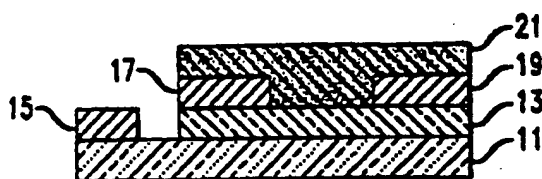
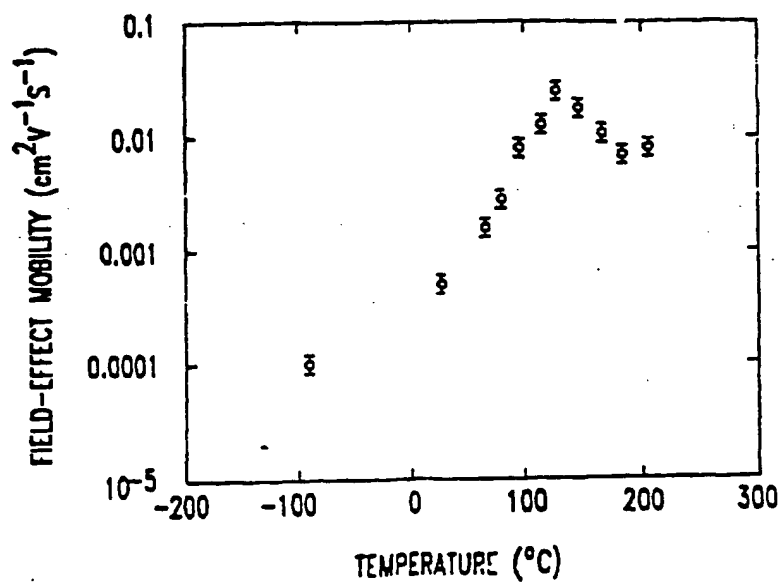
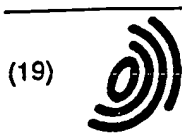


FIG. 3





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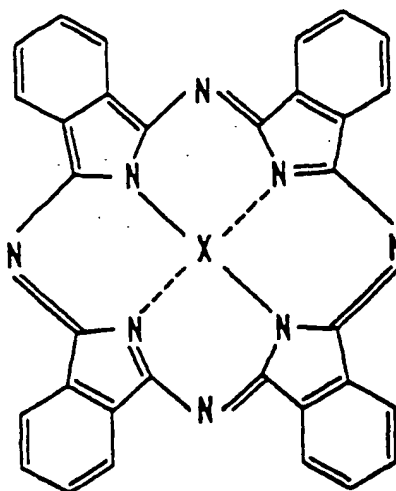
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(54) Method of making an organic thin film transistor and article made by the method

(57) Thin film transistors in which the active layer is an ordered film of a phthalocyanine coordination compound with a field-effect mobility greater than  $10^{-3}$  cm<sup>2</sup>/Vs and a conductivity in the range of about  $10^{-9}$  S/cm to about  $10^{-7}$  S/cm at 20°C are disclosed. Examples of suitable phthalocyanines include copper phthalocyanine,

zinc phthalocyanine, hydrogen phthalocyanine, and tin phthalocyanine. Thin film devices made of these materials have an on/off ratio of at least about  $10^4$ . It is advantageous if the device is fabricated using a process in which the substrate is heated to a temperature in the range of about 30°C to about 200°C when the film is formed thereon.

FIG. 1







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# EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P, X	BAO Z ET AL: "ORGANIC FIELD-EFFECT TRANSISTORS WITH HIGH MOBILITY BASED ON COPPER PHTHALOCYANINE" APPLIED PHYSICS LETTERS, vol. 69, no. 20, 11 November 1996, pages 3066-3068, XP000644040 * the whole document *	1-10	H01L51/20
X	CLARISSE C ET AL: "THE OPERATION AND CHARACTERISTICS OF DIPHthalOCYANINE FIELD EFFECT TRANSISTORS" JOURNAL OF APPLIED PHYSICS, vol. 69, no. 5, 1 March 1991, pages 3324-3327, XP000224906 * the whole document *	1	
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A	FR 2 627 629 A (MADRU ROGER) * the whole document *		
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26 January 1998	Examiner Königstein, C
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